

Redox Behaviour of β -Dihydroporphycene Cobalt Complex: Study on the Effect of the Hydrogenation of Ligand

Koichi Hashimoto,^a Taro Koide,^a Hisashi Shimakoshi,^a Yuta Hori,^b Yoshihito Shiota,^b Kazunari Yoshizawa,^b and Yoshio Hisaeda^{*,a}

^a Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University

^b Institute for Materials Chemistry and Engineering, Kyushu University

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1. General information

Reagents and solvents of best grade available were purchased from commercial suppliers and were used without further purification unless otherwise noted. Dried dichloromethane (CH₂Cl₂) was obtained by distillation from CaH₂ under a N₂ atmosphere.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 500MHz NMR spectrometer. The resonance frequencies are 500 and 125 MHz for ¹H and ¹³C, respectively. Chemical shifts were reported as δ values in ppm relative to tetramethylsilane. High-resolution electron spray ionization time-of-flight mass spectra (HR-ESI-TOF-MS) were measured on JMS-T100LC-AccuTOF and microTOFQII spectrometer (JEOL, Japan). Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra were recorded on U-3310 spectrometer (Hitachi, Japan) and V-670KS (JASCO, Japan). Electron spin resonance (ESR) measurement was carried out with a JES-FE1G X-band spectrometer (JEOL) equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter.

Redox potentials were measured by cyclic voltammetry method on an ALS electrochemical analyzer model 630C in glove box. Cyclic voltammetric measurements were carried out using 1.6 mm diameter platinum working electrode and platinum wire counter electrode

in dehydrated solvents containing 0.1 M Bu₄NPF₆ as a supporting electrolyte under nitrogen atmosphere at room temperature. In the experiment, we employed a Ag/10 mM AgNO₃ reference electrode. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with 0.1 M KCl aqueous solution.

Data from X-ray diffraction were collected by a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromator and a Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$).

The data frames were integrated using SAINT^{S1} and merged to give a unique data set for the structure determination. Absorption corrections by SADABS^{S2} were carried out. The structure was solved by a direct method and refined by the full-matrix least-squares method on all F² data using the SHELXL-97^{S3} suite of programs. All non-hydrogen atoms were anisotropically refined.

2. Synthesis

Pc and Co(II)Pc

Tetrapropyl porphycene (**Pc**) and its cobalt(II) complex (**Co(II)Pc**) were synthesized by following the reported procedure.^{S1}

Dihydroporphycene **H2Pc**^{S2}

50.8 mg (0.106 mmol) of **Pc**, *p*-toluenesulfonic hydrazide (578 mg, 3.10 mmol), and K₂CO₃ (602 mg, 4.36 mmol) were added to the 50 mL two-necked flask and the flask was substituted by nitrogen gas. 13 mL of dry pyridine was added and refluxed for 40 minutes. 40 mL of hexane was added after cooling, and the organic layer was washed 16 times with 50 mL of 5% HCl aq., 4 times with 5% NaOH aq., and 2 times with water until the layer becomes transparent. Organic layer was dried over anhydrous Na₂SO₄ and evaporated after filtration. The dihydroporphycene **H2Pc** was obtained as a purple needle crystals by recrystallization from CH₂Cl₂/hexane under N₂ in 94% yield (48.0 mg).

H2Pc was also obtained by following the reported method.^{S2}

¹H NMR (500 MHz, CDCl₃): δ 9.31 (d, $J = 11$ Hz, 1H), 8.97 (d, $J = 11$ Hz, 1H), 8.94 (d, $J = 11$ Hz, 1H), 8.86 (s, 1H), 8.84 (s, 1H), 8.68 (s, 1H), 8.19 (d, $J = 11$ Hz, 1H), 5.88 (brs, 1H), 5.00 (dd, $J = 9, 17$ Hz, 1H), 4.83 (m, 1H), 4.67 (dd, $J = 3, 17$ Hz, 1H), 3.78 (m, 6H), 3.08 (brs, 1H), 2.42 (m, 1H), 2.28 (m, 6H), 2.10 (m, 1H), 1.70 (m, 1H), 1.56 (m, 1H), 1.27 (m, 9H), 1.06 (t, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 168.37, 154.41, 143.13, 142.81, 141.27, 140.73, 138.49, 132.68, 132.40, 130.21, 127.30, 122.77, 120.46, 117.30, 114.50, 112.40, 105.72, 105.19, 48.07, 39.95,

38.50, 30.27, 30.04, 29.92, 25.53, 25.22, 25.07, 20.22, 14.53, 14.47, 14.43, 14.28.

IR (KBr, cm^{-1}): $\nu = 2954, 2927, 2869, 1609, 1561, 1496, 1463, 1367, 1257, 1209, 1177, 1083, 1042, 969, 950, 897, 811, 744$.

HR-ESI-TOF-MS: Calcd for $\text{C}_{32}\text{H}_{41}\text{N}_4$: $m/z = 481.3331$ ($[\text{M}+\text{H}]^+$). Found: $m/z = 481.3365$ ($[\text{M}+\text{H}]^+$).

UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 366 (90,100), 383 (58,300), 402 (102,200), 573 (34,600), 598 (29,600).

Elemental analysis (CHN): Calcd for $\text{C}_{32}\text{H}_{40}\text{N}_4$: C, 79.96; H, 8.39; N, 11.66%. Found: C, 79.77; H, 8.29; N, 11.54%.

Dihydroporphycene cobalt(II) complex **Co(II)H2Pc**

40.3 mg (0.0838 mmol) of dihydroporphycene **H2Pc** and cobalt(II) acetylacetonate dehydrate (302 mg, 1.10 mmol) were added to a 50 mL two-necked flask under nitrogen atmosphere. 18 mL of distilled decalin was added as a solvent, and the mixture was refluxed for 2 hours. 60 mL of hexane was added after cooling, and the organic layer was washed with 80 mL of water four times. Organic layer was dried over anhydrous Na_2SO_4 and evaporated after filtration. Crude mixture was separated by column chromatography with NH_2 modified silica gel (Wakogel 50 NH_2). The cobalt complex **Co(II)H2Pc** was obtained as a purple needle crystals by recrystallization from $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ under N_2 in 53% yield (24.1 mg).

^1H NMR (500 MHz, CDCl_3): δ 54.6, 42.9, 41.5, 38.2, 38.0, 15.0, -8.7, -19.4, -24.3, -26.9 ppm

Chemical shifts of the signals were largely shifted by the influence of the paramagnetic effect.

MS (positive mode): $\text{C}_{32}\text{H}_{38}\text{N}_4\text{Co}$ ($[\text{M}]^+$) m/z found; 537.40, calcd; 537.24

UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 382 (47900), 395 (47000), 416 (51700), 566 (21400)

Elemental analysis (CHN): Calcd. for $\text{C}_{32}\text{H}_{38}\text{N}_4\text{Co}$: C, 71.49; H, 7.12; N, 10.42%. Found: C, 71.53; H, 7.06; N, 10.46%.

CH₃Co(III)H2Pc-A and **CH₃Co(III)H2Pc-B**

The electro-synthesis of **CH₃Co(III)H2Pc-A** and **CH₃Co(III)H2Pc-B** was performed under N_2 atmosphere and in the dark using the following procedure: **Co(II)H2Pc** (1 mM) and CH_3I (50 mM) were dissolved in dry DMF containing 1 mM TBABF₄. Bulk electrolysis of the solution was performed at -1.2 V vs. Ag/AgCl using a divided cell system consist of a platinum mesh electrode as working, a zinc plate electrode as counter (sacrificial). After completion of electrolysis, the solution was transferred from the cell and the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in $\text{DMF-}d_7$ and ^1H NMR was measured.

CH₃Co(III)H₂Pc-A and **CH₃Co(III)H₂Pc-B** (as a crude mixture)

¹H NMR (500 MHz, DMF-*d*₇): δ 8.2-9.3 (m), -3.97 (s, 3H), -4.04 (s, 3H)

MS (positive mode): C₃₃H₄₁N₄Co ([M]⁺) *m/z* found; 552.26, calcd; 552.27

UV/Vis (DMF): λ_{max}/nm: 396, 584

3. ^1H NMR spectra

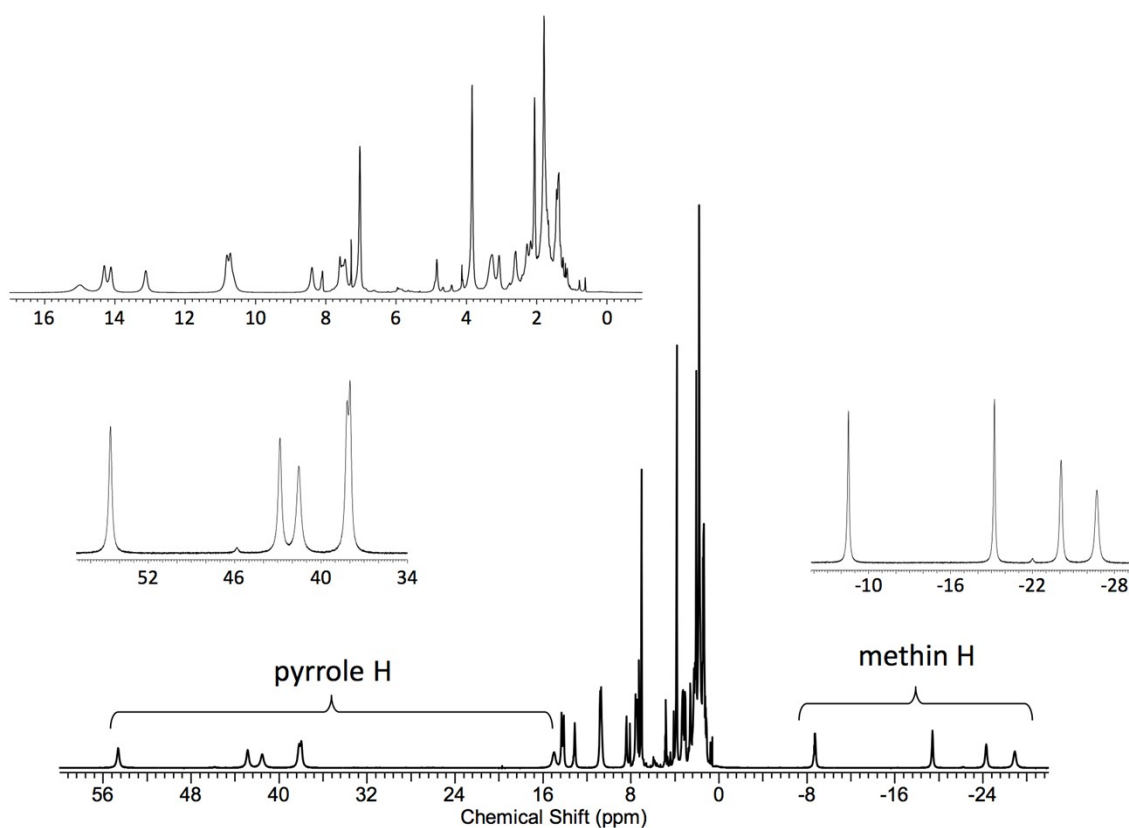
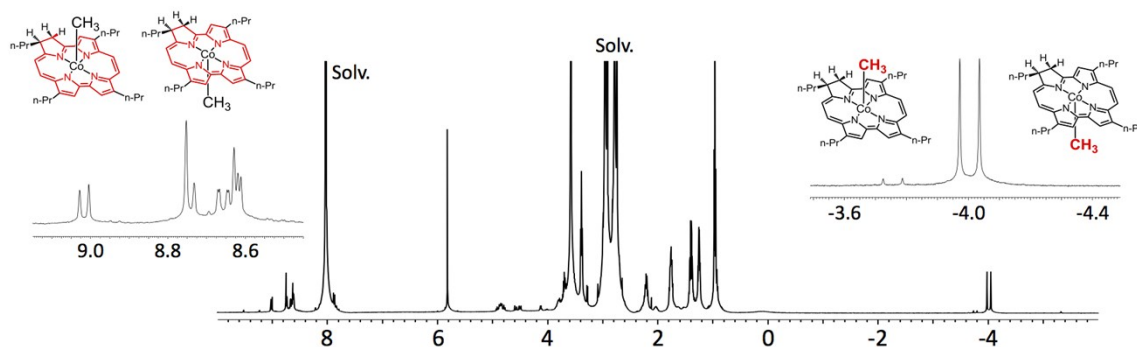


Figure S1. ^1H NMR spectrum of $\text{Co(II)H}_2\text{Pc}$ in CDCl_3 .

(a)



(b)

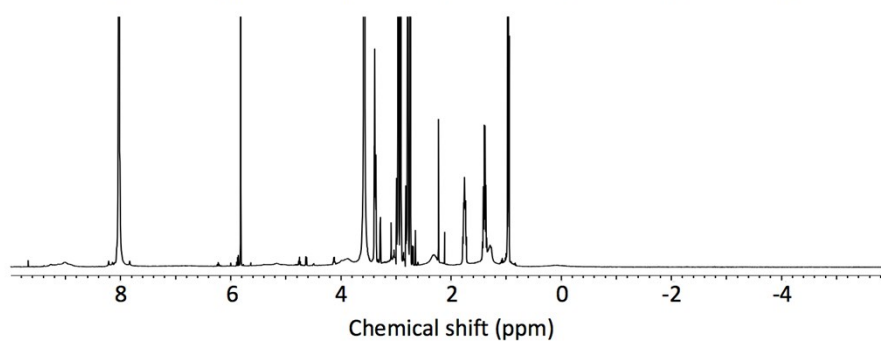


Figure S2. ^1H NMR spectrum of $\text{CH}_3\text{Co(II)H}_2\text{Pc-A}$ and -B in $\text{DMF-}d_7$. a) after electrochemical synthesis, b) after irradiation of light.

4. Cyclic Voltammogram

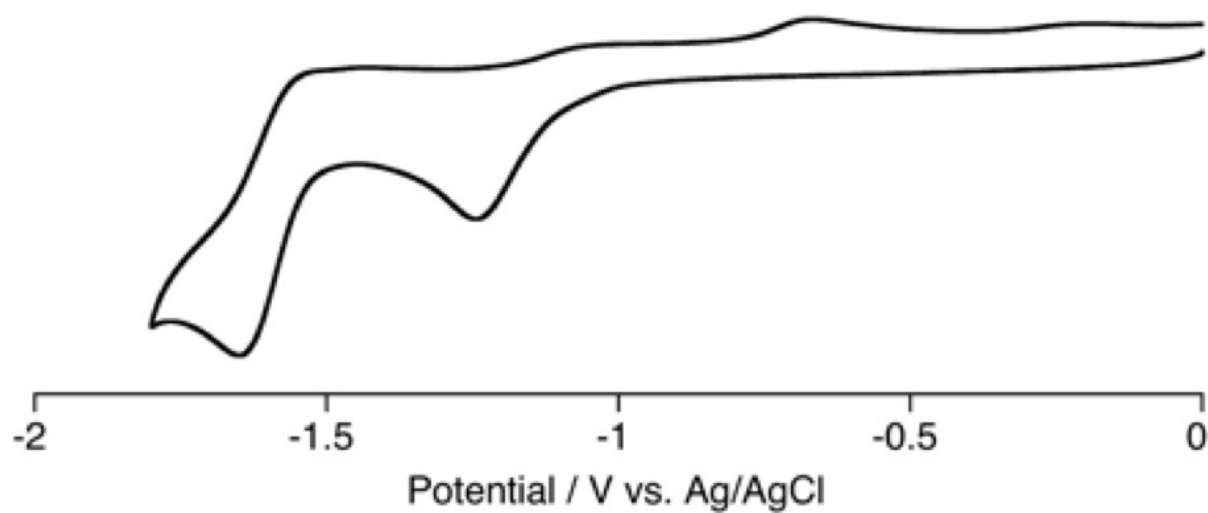


Figure S3. Cyclic voltammogram of **Co(II)H₂Pc** under electrochemical reductive condition in PhCN with CH₃I. All the data were collected under N₂. Supporting electrolyte: 0.1 M TBAPF₆, scan rate: 0.1 V/s, WE: Pt, CE: Pt, RE: Ag/Ag.

5. Spectroelectrochemical measurement

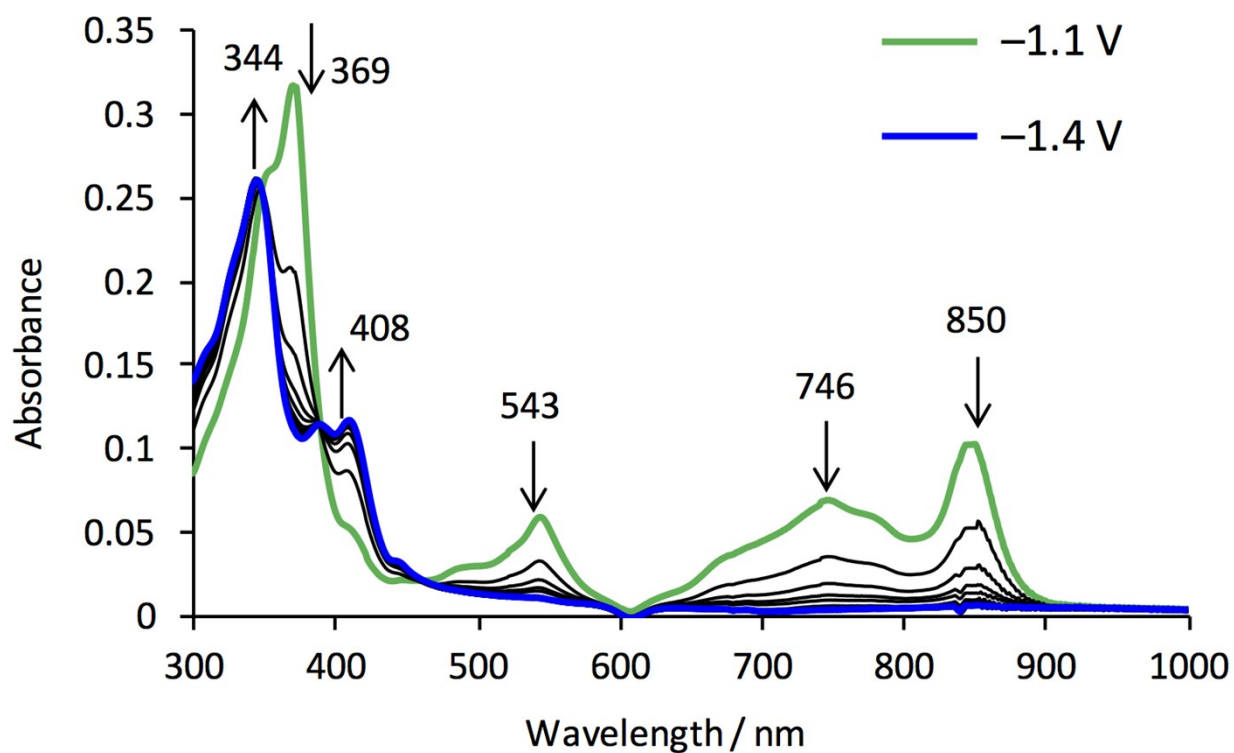
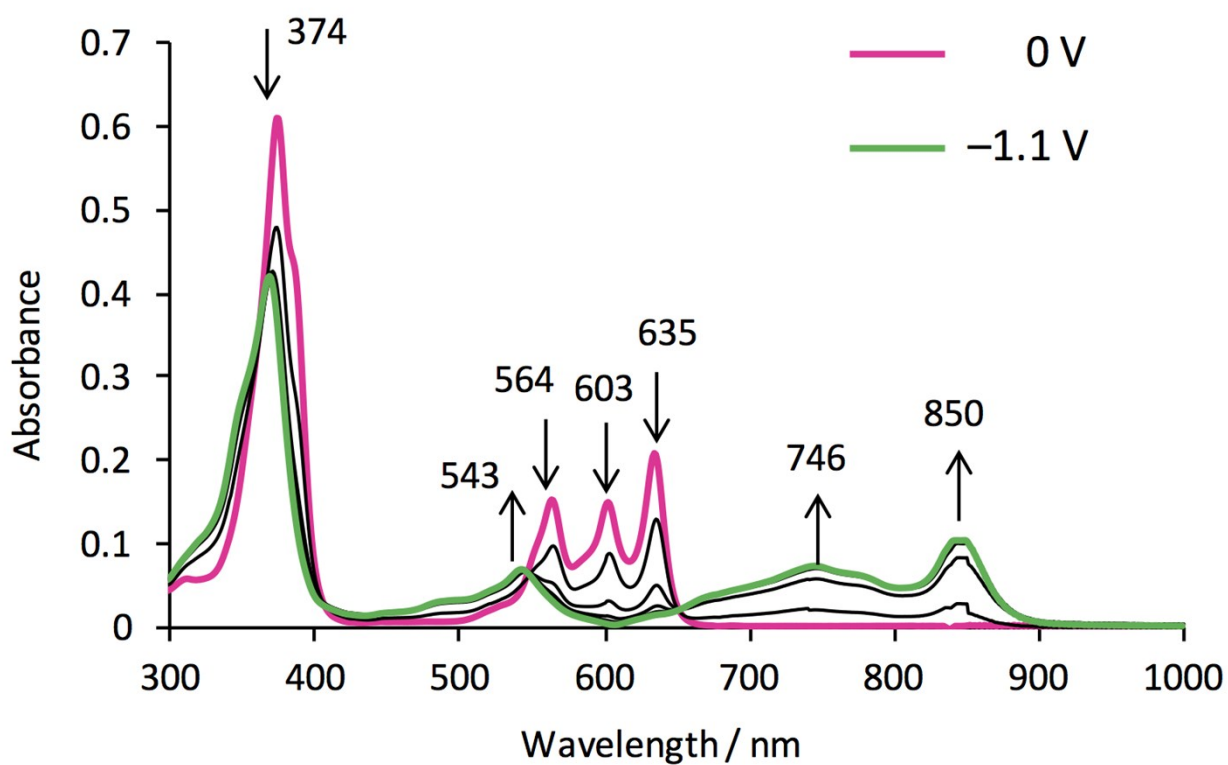


Figure S4. Time-resolved UV-vis absorption spectra for the reduction of **Pc** in PhCN +0.1 M TBAPF₆ at a controlled potential of -1.1 V and -1.4 V, which correspond to the first and second reduction steps, respectively.

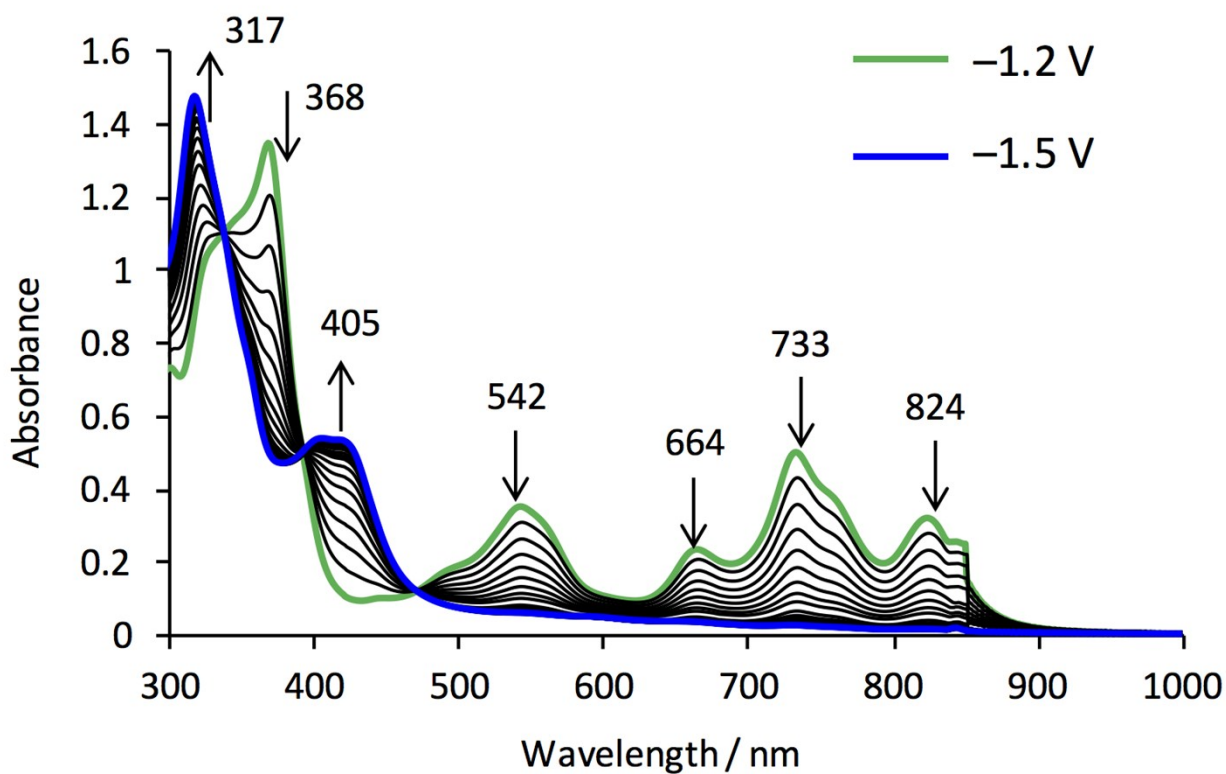
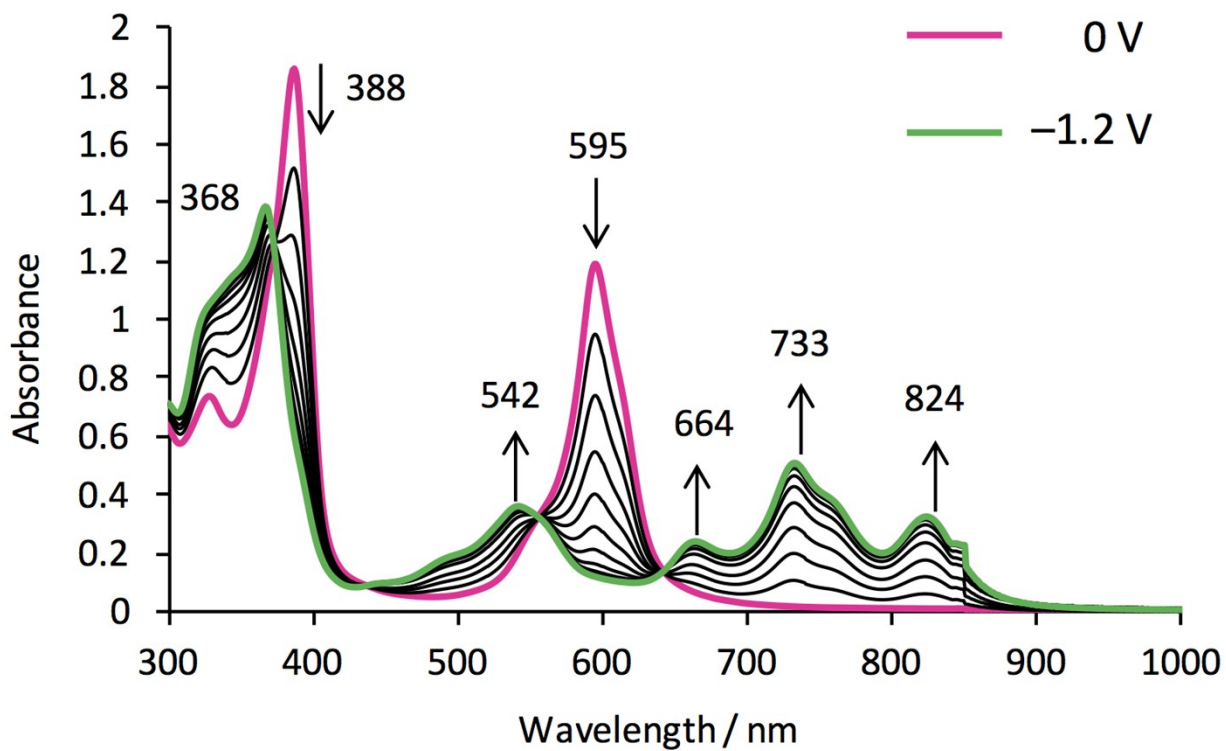


Figure S5. Time-resolved UV-vis absorption spectra for the reduction of Co(II)Pc in PhCN + 0.1 M TBAPF₆ at a controlled potential of -1.2 V and -1.5 V, which correspond to the first and second reduction steps, respectively.

6. EPR spectra

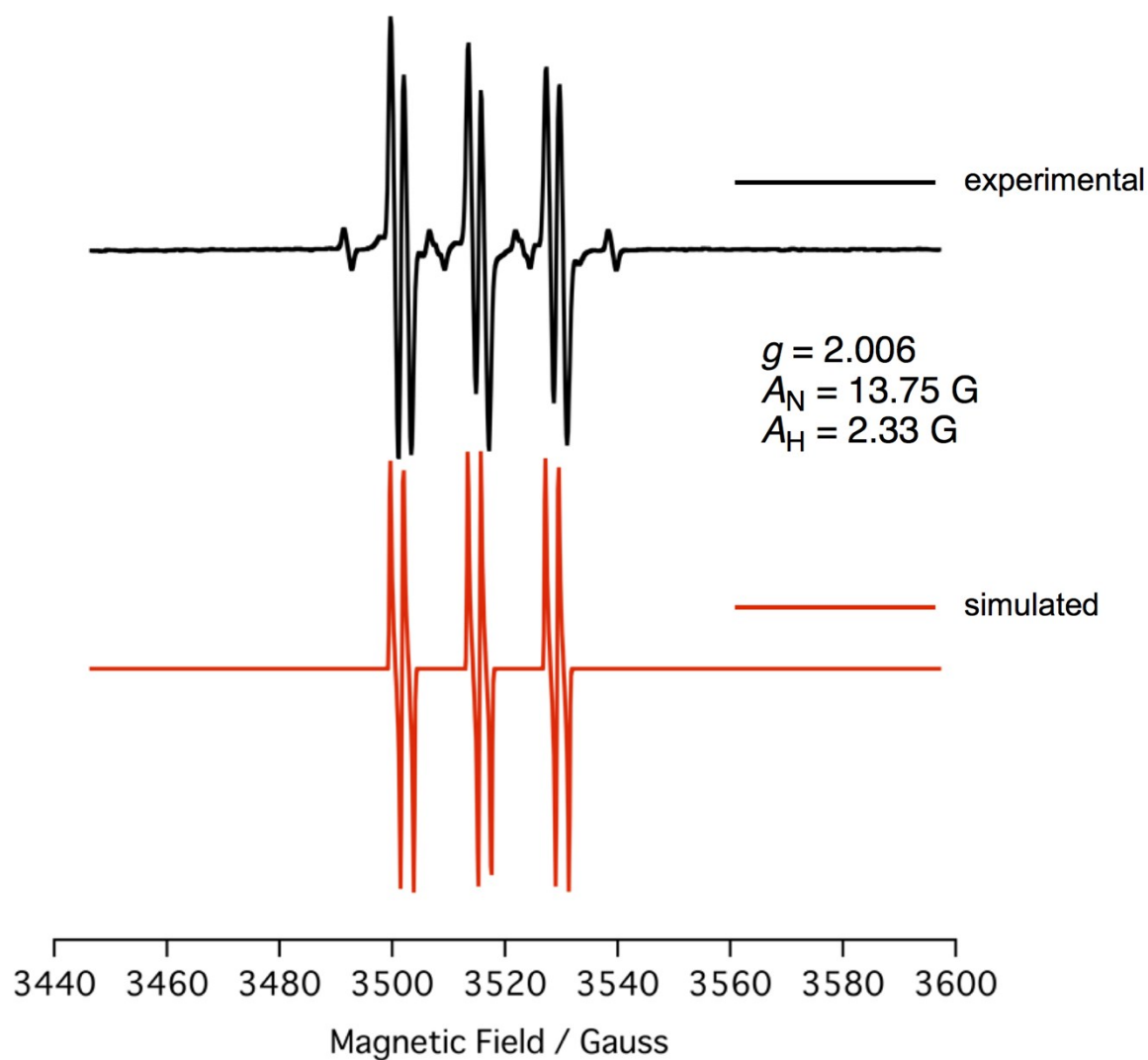


Figure S6. EPR spectra of **PBN-CH₃ radical** generated by the light irradiation to the solution of **CH₃-Co(III)H₂Pc** in DMF; before light irradiation (black) and after light irradiation (red line). $g = 2.006$, $A_N = 13.75 \text{ G}$, $A_H = 2.33 \text{ G}$.

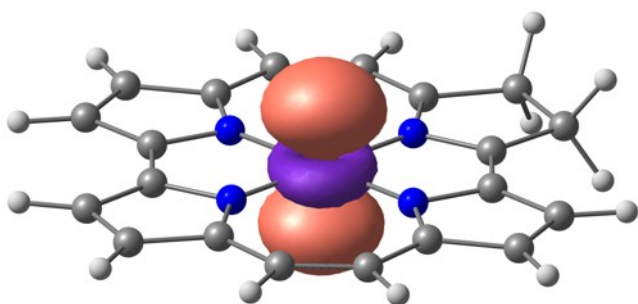
7. DFT calculation

We optimized the structures of non-hydrogenated and hydrogenated porphycene species using the DFT calculations with the B3LYP functional^{S3} implemented by the Gaussian 16 package.^{S4} We used the Wachters-Hay^{S5} for Co atom and D95** basis set^{S6} for C, N, and H atoms. Vibration frequencies were computed in order to confirm that the optimized geometries have no imaginary frequency.

Figure S7 shows calculated HOMO of one-electron reduced species of **Co(II)H2Pc** in the closed-shell singlet state and α -SOMO in the triplet state. Since the HOMO in the closed-shell singlet state is assigned to be cobalt metal center, we can confirm that the one-electron reduced species in the closed-shell singlet state corresponds to the cobalt reduced species, **Co(I)H2Pc⁻**. On the other hand, one-electron reduced species in the triplet and open-shell singlet states corresponds to the ligand reduced species, **Co(II)H2Pc⁻**, because the α -SOMO in the triplet state is assigned to be the ligand moiety.

To investigate the dependency of DFT functionals, we also calculated by using the B3LYP*,^{S7} CAM-B3LYP,^{S8} BP86,^{S9} and ω B97X^{S10} functionals and B3LYP with 6-311+G** basis.

(a)



(b)

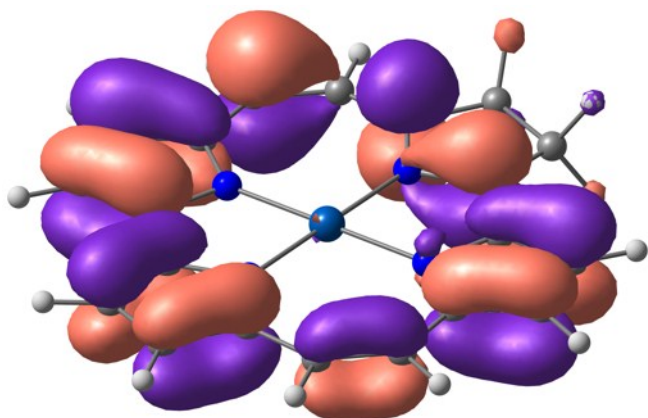
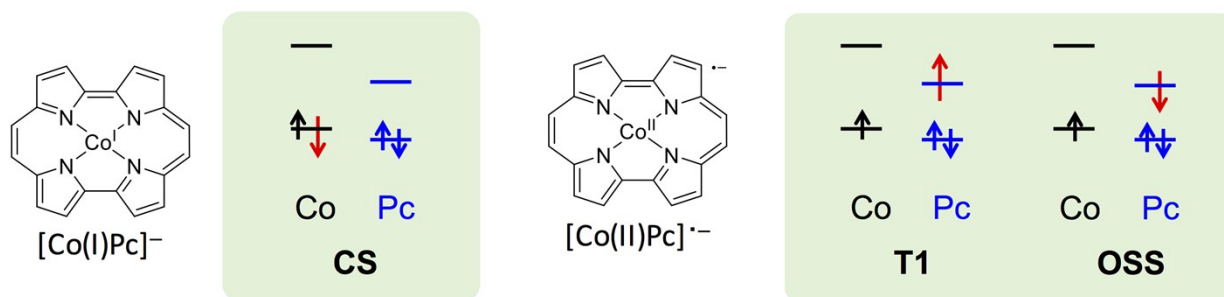


Figure S7. Calculated (a) HOMO of **Co(I)H2Pc⁻** in the closed-shell singlet and (b) α -SOMO **Co(II)H2Pc⁻** in the triplet state at the B3LYP level.

Program: Gaussian 16

Basis set: Co: Wachters-Hay Others: D95**



(kcal/mol)

B3LYP	CS	T1	OSS	B3LYP*	CS	T1	OSS	BP86	CS	T1	OSS
CoPc	21.1	0.0	0.1	CoPc	16.4	0.0	0.0	CoPc	3.6	0.0	-0.6
CoH2Pc	7.7	0.0	0.1	CoH2Pc	3.7	0.0	0.0	CoH2Pc	-5.7	0.0	-5.9
CAM-B3LYP	CS	T1	OSS	ω B97X	CS	T1	OSS	B3LYP ^[1]	CS	T1	OSS
CoPc	30.3	0.0	0.2	CoPc	33.8	0.0	0.2	CoPc	21.0	0.0	0.1
CoH2Pc	17.0	0.0	-0.1	CoH2Pc	17.3	0.0	0.2	CoH2Pc	7.6	0.0	0.1

^[1] basis set: 6-311+G**

Figure S8. Electronic structures and calculated energies of the two possible one-electron reduced species, the cobalt reduced ones and the ligand reduced ones, of **Co(II)Pc** and **Co(II)H2Pc**. Three different spin states, the closed-shell singlet (**CS**), triplet (**T1**), and open-shell singlet (**OSS**) states, were taken into account in the one-electron reduced species.

Table S1. Cartesian coordinates of **Co(II)Pc** in the close-shell singlet state.

angstrom			
Atom	x	y	z
Co	0.000130	0.000000	-0.000001
N	1.434229	1.289236	-0.000073
N	-1.434581	1.289006	-0.000054
C	0.695544	3.689999	-0.000104
H	1.156966	4.678242	-0.000114
C	1.644343	2.639685	-0.000096
C	-0.695611	3.689730	-0.000063
H	-1.157319	4.677885	-0.000018
C	2.682499	0.699525	-0.000049
C	3.076104	2.903254	-0.000084
C	-2.682841	0.699454	-0.000035
C	3.726008	1.688585	-0.000073
H	4.792483	1.494877	-0.000070
C	-1.644436	2.639565	-0.000032
C	-3.076241	2.903131	0.000095
C	-3.726289	1.688496	-0.000056
H	-4.792700	1.494692	-0.000077
N	-1.434483	-1.289112	0.000058
N	1.434330	-1.289133	0.000059
C	-0.695326	-3.689780	0.000080
H	-1.156963	-4.677967	0.000049
C	-1.644231	-2.639687	0.000025
C	0.695828	-3.689948	0.000140
H	1.157323	-4.678157	0.000171
C	-2.682787	-0.699653	0.000008
C	-3.076017	-2.903362	-0.000061
C	2.682554	-0.699325	0.000039
C	-3.726159	-1.688778	-0.000062
H	-4.792585	-1.495055	-0.000120
C	1.644552	-2.639564	0.000123
C	3.076332	-2.903023	0.000071
C	3.726141	-1.688303	0.000142

H	4.792601	-1.494515	0.000185
H	3.519783	3.894019	-0.000101
H	-3.519876	3.893978	0.000192
H	-3.519576	-3.894243	-0.000115
H	3.520089	-3.893753	0.000074

Table S2. Cartesian coordinates of **Co(II)Pc⁻** in the triplet state.

Atom	angstrom		
	x	y	z
Co	0.000000	0.000000	0.000001
N	-1.435524	-1.301142	0.000088
N	1.435514	-1.301153	0.000016
C	-0.688851	-3.719774	-0.000003
H	-1.155746	-4.705248	-0.000040
C	-1.646843	-2.664430	-0.000013
C	0.688823	-3.719779	0.000027
H	1.155710	-4.705257	0.000087
C	-2.678147	-0.710375	0.000056
C	-3.055755	-2.918142	-0.000267
C	2.678142	-0.710395	-0.000034
C	-3.707376	-1.684140	0.000115
H	-4.773305	-1.488334	0.000215
C	1.646823	-2.664442	0.000010
C	3.055733	-2.918165	0.000272
C	3.707363	-1.684167	-0.000257
H	4.773294	-1.488370	-0.000458
N	1.435524	1.301142	-0.000088
N	-1.435514	1.301153	-0.000015
C	0.688851	3.719774	0.000003
H	1.155746	4.705248	0.000045
C	1.646843	2.664430	0.000012
C	-0.688823	3.719779	-0.000027
H	-1.155710	4.705256	-0.000081
C	2.678147	0.710375	-0.000058

C	3.055755	2.918142	0.000276
C	-2.678142	0.710395	0.000032
C	3.707376	1.684140	-0.000128
H	4.773305	1.488334	-0.000236
C	-1.646823	2.664442	-0.000011
C	-3.055733	2.918165	-0.000257
C	-3.707363	1.684167	0.000242
H	-4.773294	1.488370	0.000432
H	-3.504175	-3.906111	-0.000467
H	3.504146	-3.906138	0.000485
H	3.504175	3.906111	0.000483
H	-3.504146	3.906138	-0.000457

Table S3. Cartesian coordinates of **Co(II)H2Pc** in the close-shell singlet state.

Atom	Angstrom		
	x	y	z
Co	-0.040941	0.008821	-0.000016
N	1.715813	-0.802711	-0.000042
N	-1.065107	-1.638347	-0.000002
C	1.669165	-3.303805	0.000034
H	2.389679	-4.123335	0.000019
C	2.275528	-2.050871	0.000013
C	0.321157	-3.719123	0.000047
H	0.180015	-4.800575	-0.000013
C	2.719729	0.133825	-0.000015
C	3.807055	-1.970947	-0.000032
C	-2.416769	-1.432858	0.000018
C	4.106918	-0.457101	0.000045
H	4.677809	-0.140871	-0.882675
C	-0.878472	-3.004602	0.000053
C	-2.175499	-3.663917	-0.000313
C	-3.137120	-2.677868	0.000305
H	-4.215541	-2.790801	0.000545
N	-1.794780	0.830181	0.000045

N	0.946691	1.663614	0.000003
C	-1.773494	3.350072	-0.000024
H	-2.502019	4.162411	-0.000079
C	-2.384061	2.072454	-0.000022
C	-0.446204	3.754048	0.000002
H	-0.285454	4.832556	0.000047
C	-2.822722	-0.084206	0.000040
C	-3.823210	1.919280	-0.000341
C	2.320099	1.454984	-0.000002
C	-4.097428	0.562845	0.000194
H	-5.064999	0.073291	0.000367
C	0.763452	3.012222	-0.000013
C	2.061102	3.679503	0.000313
C	3.032366	2.705737	-0.000222
H	4.109667	2.832759	-0.000402
H	4.223112	-2.474153	0.882014
H	-2.322463	-4.739405	-0.000565
H	-4.531887	2.741480	-0.000593
H	2.198938	4.756232	0.000554
H	4.677662	-0.140936	0.882886
H	4.223020	-2.474019	-0.882200

Table S4. Cartesian coordinates of **Co(II)H₂Pc^{•-}** in the triplet state.

	angstrom		
Atom	x	y	z
Co	-0.058858	0.000538	0.000010
N	1.854906	-0.531523	-0.000025
N	-0.773522	-1.802633	0.000012
C	2.204028	-3.020078	-0.000024
H	3.053115	-3.706502	-0.000005
C	2.605424	-1.680086	-0.000032
C	0.956868	-3.646425	-0.000004
H	0.985902	-4.735904	0.000055
C	2.653188	0.554218	-0.000009

C	4.098053	-1.328984	-0.000064
C	-2.152117	-1.817708	0.000008
C	4.123632	0.219207	0.000064
H	4.627231	0.636300	-0.882184
C	-0.362853	-3.128272	0.000001
C	-1.516923	-3.967293	0.000230
C	-2.647349	-3.136492	-0.000154
H	-3.691505	-3.426977	-0.000293
N	-1.919579	0.537591	0.000028
N	0.648048	1.812121	0.000008
C	-2.302727	3.050548	-0.000012
H	-3.160149	3.725469	0.000000
C	-2.704926	1.676033	-0.000021
C	-1.077200	3.664054	-0.000002
H	-1.090794	4.754232	-0.000025
C	-2.780093	-0.532847	0.000001
C	-4.076284	1.293279	0.000159
C	2.034892	1.814765	0.000014
C	-4.125560	-0.108416	-0.000208
H	-4.999876	-0.748888	-0.000370
C	0.255046	3.128987	0.000017
C	1.410093	3.966591	-0.000166
C	2.538750	3.136500	0.000133
H	3.583299	3.427236	0.000226
H	4.599179	-1.748194	0.882012
H	-1.490623	-5.052108	0.000395
H	-4.910620	1.987097	0.000291
H	1.385229	5.051224	-0.000307
H	4.627090	0.636149	0.882467
H	4.599088	-1.748033	-0.882272

8. Supporting references

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